Temperature dependence of the resistivity of amorphous Mn thin films

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Temperature dependence of the resistivity of amorphous Mn thin films

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Abstract

Resistivity measurements on an amorphous Mn thin film have been performed over the temperature range from 1.5 to 300 K. The films were prepared by thermal evaporation on glass substrates held at liquid-nitrogen temperature in an ambient pressure of $2 \times 10^{-5}$ Torr. The amorphous nature of the film has been verified by high-voltage electron microscopy. The resistivities are large, typically of the order of 4.00 $\mu$Ω m or higher with small high-temperature slopes which are negative. At low temperatures ($T < 10 \text{ K}$) the resistivity obeys a $T^2$ law. These results can be understood in terms of a model based on temperature dependent structure factor as suggested by Nagel. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The crystal structure of $\alpha$-Mn is extremely complicated. It has a bcc structure with 29 atoms per unit cell in two clusters, in a $Td^3 - 143m$ space group and is stable up to 700°C [1]. These atoms are distributed over four crystallographically equivalent sites: (i) two atoms at $(0 \ 0 \ 0) + \text{bcc}$ with point symmetry $43m$, (ii) eight atoms at $(x \ x \ x) + \text{bcc}$ with point symmetry $3m$, (iii) 24 atoms at $(x \ x \ z) + \text{bcc}$ with point symmetry $m$, and (iv) 24 atoms at $(x \ x \ x) + \text{bcc}$ with point symmetry $m$ [2]. These sites are subsequently referred to as sites I, II, III and IV, respectively.

The resistivity–temperature behavior of $\alpha$-Mn thin films is extremely anomalous [3]. The behavior typical of a highly disordered, near-glass-like metallic material is obtained at low substrate temperatures and in poor vacua. [4].

It has been reported [5] that the electrical properties of amorphous alloys compare more closely to liquid than to crystalline metals; the high degree of atomic disorder is evident in the magnitude of the resistivity, $\rho$ typically 3.50 $\mu$Ω m, and its slow variation in temperature. Further, at high temperatures ($\partial \rho/\partial T$) is negative for some amorphous alloys, which is also characteristic of liquid rather than crystalline metals. At low temperatures almost all amorphous alloys show a region where $\rho$ varies as $-\ln T$ [6,7]. High resolution resistivity measurements on a wide variety of amorphous alloys have been reported for the temperature range from 0.5 to 300 K by Cochrane and Strom-Olsen [8]. At low temperatures, below 20 K, the resistivity is found to be dominated by a $-\ln (T^2 + A^2)$ term with $A \sim 0.5 \text{ K}$.

The purpose of this communication is to point out that the resistivity–temperature behavior of

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amorphous Mn metal is analogous in certain respects to the behavior of some amorphous alloys [5].

2. Experimental details

The starting material was 99.98% electrolytic manganese. The flakes were first cleaned with 5% HCl in methanol to remove surface oxides and other contaminants. They were then dried and ground to fine powder and loaded into a molybdenum boat for vacuum deposition. The substrate was held in a brass mask whose temperature was kept at about 77 K. This was done by incorporating a liquid N\textsubscript{2} trap (made of copper tubing) to lie on top of the mask. The liquid N\textsubscript{2} as a coolant from a transport dewar was run through an inlet of the copper tube from time to time through the N\textsubscript{2} trap and consequently came out of an outlet. In this way, the substrate attained the liquid-nitrogen temperature. At such substrate temperatures, the unit was pumped down for about six hours until an ambient pressure of 2 \times 10^{-5} Torr was obtained as measured with an ion gauge fitted to the coating unit. The pressure was kept constant during evaporation at about 2 \times 10^{-5} Torr. The thickness of the film was monitored by a quartz crystal monitor. For actual film thickness measurement, an interferometer was used. The substrate temperature was measured with a copper-constantan thermocouple and the deposition rate was kept at 12 As\textsuperscript{-1}. Resistivity measurements were made by the van der Pauw [9] four probe technique in a conventional He\textsuperscript{4} cryostat. Temperatures below 4.2 K were obtained by condensing liquid helium into the insert of the cryostat and pumping on it. Temperatures between 300 and 60 K were measured with a copper resistance thermometer. For temperatures below 60 K an Allen-Bradley sensing resistor was used. This has a resistance of about 200 \Omega at 25 K and rises to about 300 \Omega at 4.2 K. This sensor is therefore sensitive for temperatures below 4.2 K.

3. Results

The temperature variation of the resistivity of the amorphous film and that of the crystalline film studied by Boakye and Grassie [4] is presented in Fig. 1(a) and (b), respectively. It can be seen from the results that the temperature variation of the resistivity of the amorphous specimen is different from that of the crystalline sample which was deposited on a glass substrate held at 573 K in an ambient pressure of 10^{-6} Torr [4]. In the case of the amorphous film, there is first a gradual increase in resistivity as the temperature is dropped from 300 to about 70 K. The resistivity then increases sharply reaching an excess resistivity of 5.20 \mu\Omega m as compared with 0.80 \mu\Omega m for the crystalline sample. The slope of the \rho versus T curve of the amorphous sample is -0.42 \times 10^{-8} \mu\Omega m K\textsuperscript{-1} at room temperature whilst that of the crystalline sample is 2.05 \times 10^{-10} \mu\Omega m K\textsuperscript{-1}. The electron diffraction patterns of the two specimens are presented in Plate 1(a) and (b). An analysis [4] of the diffraction rings in Plate 1(a) revealed the crystalline nature of the film with a lattice constant.
of 8.91 Å. A diffuse diffraction pattern is observed in Plate 1(b), revealing the amorphous nature of this specimen. Size effects are not observed in these films whose thicknesses are in the 3000–4000 Å range. This is because the mean free path of the conduction electrons, for resistivities of 1.40 μΩ m typical of the bulk α-Mn, is estimated [10] to be not more than 1.33 Å even if we assume that the five d electrons per atom have a high effective mass as is suggested by the low temperature specific heat [11] and the Hall effect measurements [10] and that the two s electrons are nearly free electron like, as is the case in the band structure calculation [12] for γ-Mn, the only band structure available for manganese.

4. Discussion

Ziman [13] has calculated the temperature dependence of resistivity using a formalism [5] primarily derived for simple liquid crystals. Evans et al. [14] have extended this to include liquid transition metals and Sinha [15] has suggested that this theory could be applied to metallic alloy glasses. In applying this theory to the glass, the temperature dependence is included as in the case of the liquid by taking into account the change in the shape of the structure factor S(k) as T is varied. Nagel [16] has suggested that in order to get an estimate of the importance of this effect on the resistivity, a calculation must be made starting from a microscopic model of the glass. In a liquid, S(k) will depend quite strongly on temperature and can be calculated using the Percus–Yevick equations [17].

A similar model has been used to describe the glass. However, in the solid, the change in S(k) should be calculated as due to the vibration of ions around their equilibrium positions.

For a transition-metal system like Mn, the resistivity can be expressed as [16]

$$\rho = \frac{30\pi^2 h}{me^2 k_F^2 E_F \Omega} \sin^2 \left[ \eta^2 (E_F) \right] S(2k_F),$$

where $k_F$ and $E_F$ are the Fermi wave vector and energy, respectively and $\Omega$ is the atomic volume. $\eta^2 (E_F)$ is the d wave phase shift describing the scattering of the conduction electrons of energy $E_F$ by the ion cores which each carry a muffin-tin potential. The temperature dependence of $\rho$ is therefore determined by the temperature dependence of $S(2k_F)$. From the above expression Nagel [16] has obtained an expression for the resistivity given by

$$\rho = \frac{30\pi^2 h}{me^2 k_F^2 E_F \Omega} \sin^2 \left[ \eta^2 (E_F) \right] \times \{ 1 + [S_0 (2k_F) - 1] \exp \{ -2[\omega(T) - \omega(0)] \} \},$$

where the phonon frequency $\omega(T)$ can be obtained from the Debye approximation.

The temperature coefficient of resistivity is given by Ref. [16]

$$\alpha = 1/\rho (\delta \rho / \delta T)$$

$$\approx 2[1 - S_T (2k_F)] / S_T (2k_F) |\delta \omega(T)/\delta T|,$$

where the smooth line is to act as a guide to the eye.
Table 1.
Results from amorphous Mn thin film

<table>
<thead>
<tr>
<th></th>
<th>Ambient pressure (Torr)</th>
<th>Substrate temperature $T_s$ (K)</th>
<th>Deposition rate (Å s$^{-1}$)</th>
<th>Film thickness (Å)</th>
<th>$\rho_{900}$ (μΩ m)</th>
<th>$\rho_{9}$ (μΩ m)</th>
<th>Slope at 300 K (Ω m K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous sample</td>
<td>$2 \times 10^{-5}$</td>
<td>77</td>
<td>12</td>
<td>3000</td>
<td>4.20</td>
<td>5.20</td>
<td>$-0.42 \times 10^{-8}$</td>
</tr>
<tr>
<td>Crystalline sample</td>
<td>$10^{-6}$</td>
<td>573</td>
<td>7</td>
<td>3400</td>
<td>1.40</td>
<td>0.61</td>
<td>$2.05 \times 10^{-10}$</td>
</tr>
<tr>
<td>Boakye and Grassie [4]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Equations (2) and (3) are theoretical deductions by Nagel [16]. Eq. (2) cannot be evaluated absolutely in view of the structure factor $S_0(2k_F)$ which has not been calculated and the exponent term which contains the Debye–Waller factor which is a function of $T^2$ at low temperatures. In spite of the above difficulties, a rough estimate can be made for the resistivity. If $k_F$ and $E_F$ for Mn are taken as $1.70 \times 10^{10}$ m$^{-1}$ and 10.9 eV, respectively [18], and the effective mass is taken [18] as $m^* = 27$ m, then substitution of $m^*$ for $m$ in Eq. (2) gives an estimate of the resistivity at room temperature to be 5.00 μΩ m. This is on the assumption [16] that the scattering angle is extremely small [16]. Eq. (3) explains the negative slope of the coefficient of resistivity $\kappa$. In the Debye approximation, since $\text{d} \ln \rho / \text{d} k > 0$, $\kappa$ will be negative if $S_F(2k_F) > 1$ even at high temperatures. The above Eqs. (2) and (3) are therefore deductions to assist in the explanation of the behavior of the resistivity–temperature curve of Fig. 1(a). These are not plotted in view of the reasons given above.

Accordingly, the present results may be interpreted by suggesting that: the random structure smears out the peak in the radial distribution function that coincides with the $2k_F$ dimension of the Fermi surface and hence leads to a decrease in the resistivity associated with the Debye–Waller factor. This causes the temperature dependence to change from a $T^2$ dependence at temperatures low in comparison to the Debye temperature to a linear $T$ dependence at high temperatures. A plot of the resistivity $\rho$ versus $T^2$ of the sample under investigation at low temperatures ($T < 10$ K) supports this hypothesis. This plot is presented in Fig. 2.

A summary of the results of measurements on the amorphous Mn thin film and the results of measurements on the crystalline sample by Boakye and Grassie [4] is given in Table 1 for purposes of comparison.

5. Conclusion

In conclusion, the amorphous metallic glass state of Mn thin films has resistivities that are high with high-temperature slopes that are negative. At low temperatures, the resistivity obeys a $T^2$ law. This interpretation is in agreement with the work of Nagel [16].

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